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Tests of a Mechanism for H₂S Release during Coal Pyrolysis

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Abstract

We have used a temperature programmed, gas evolution technique to compare H₂S from coal and from pyrite in the presence of minerals or polymers. Pyrite decomposition in coal with H₂S release can be observed directly only if carbonate minerals, particularly iron-containing carbonates, are absent. Two distinct chemical mechanisms are required to model conversion of pyrite in coal to H₂S and pyrrhotite. Initially a reaction at pyrite grain surfaces (shrinking core model) occurs that is controlled by the rate of iron movement toward crystallite centers and by hydrogen-donor availability. Tar evolution (as indicated by methane-plus-ethane) also requires H-donors. Organic free radicals compete so efficiently for this scarce commodity that the rate of pyrite decomposition slows. At a 10 K/min heating rate, the rate of H₂S release by the H-donor mechanism reaches a maximum at 700 K and then decreases. Unimolecular decomposition of coal pyrite to FeS and S₂ then occurs sharply at 830 K. Coal pyrolysis products effectively capture S₂, and the rate of H₂S release matches that of sulfur release from pure pyrite in a vacuum (0.07 mg-S/cm²/min at 773 K). The high temperature H₂S evolution peak from coal is often distorted by inorganic sulfide hydrolysis and reversible H₂S capture, both of which depend on a rapidly changing [H₂S]:[H₂O] ratio. Water release from clays affects H₂S evolution. By monitoring CO₂, H₂O, and CH₄-plus-C₂H₆ as well as H₂S, we can provide a consistent picture for a particularly difficult case, the Illinois #6 coal from the set of Argonne coals. Modified Ill #6 coal (acid-leached or pyrite-free), spiked samples, and polymers were pyrolyzed with inert or reactive gas sweeps to provide supporting data.

Introduction

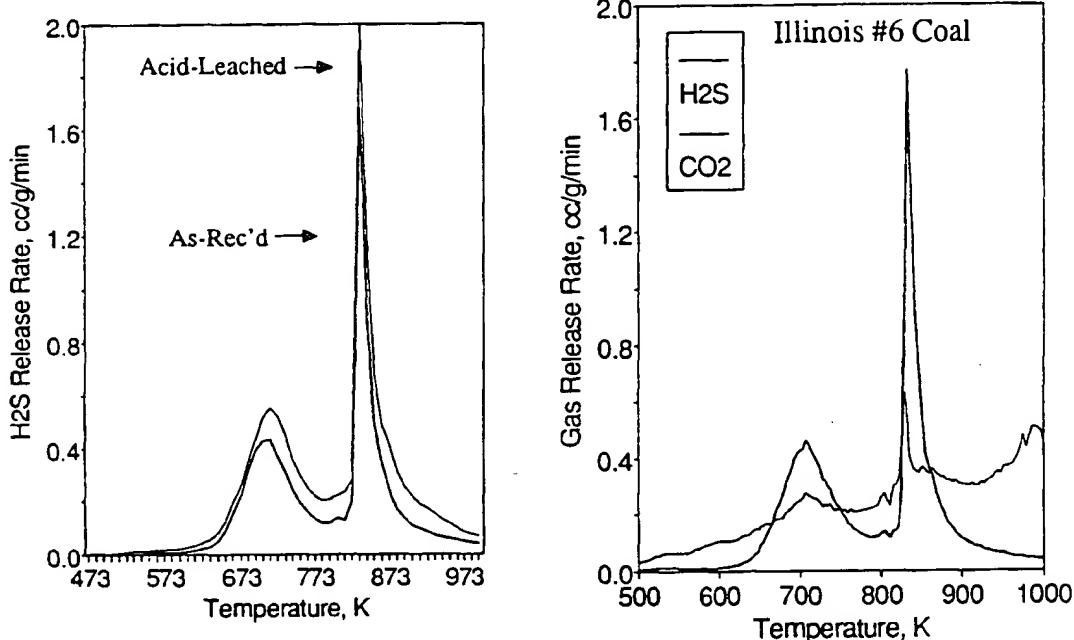
The release of sulfur-containing compounds from coals during pyrolysis has been of continuing interest in our laboratory and others. The volume of literature on this subject is great and occasionally contradictory. The choice of authorities can bias introductory comments. Oh et al.¹ have summarized literature preferences from our laboratory. In general, our biases match those of Khan.²

Hydrogen sulfide is the principal sulfur species released during coal pyrolysis. Illinois #6 coal from the set of Argonne coals, probably the best characterized high sulfur coal available,³ was chosen to test our understanding of coal sulfur chemistry. We used a procedure for temperature programmed gas evolution (at 10 K/min) somewhat similar to the TGA/MS and TGA/FTIR used by others.^{4,5} We used a small all-quartz pyrolysis tube, a large sample size (0.5 g), and argon sweep at 20 cc/min. A quadrupole MS detected H₂S and other gases; no weight changes were recorded.¹ Conditions were varied, and conclusions that follow are based on the gas evolution data.

Results and Discussion

Figure 1 shows release of H₂S from as-received and from acid-leached Illinois #6 coal. Capture of H₂S by carbonate minerals often interferes with its detection; this

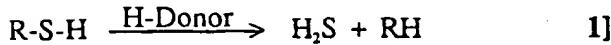
reaction has rarely been adequately appreciated. Only a weak acid treatment is needed to remove mineral carbonates (we used 5% acetic acid) but enough time to wet the particle completely must be allowed (18 hr at 373 K). Figure 2 shows that CO_2 release during coal pyrolysis matches H_2S release, as one would expect if carbonate minerals react with H_2S . Thermodynamics for H_2S capture by calcite or dolomite is borderline at best, and our spiking experiments proved these minerals ineffective, as shown previously.²⁶ Apparently the iron component captures H_2S . Ankerite (ferroan dolomite), siderite, and synthetic FeCO_3 were all reactive, but only ankerite had sufficient thermal stability to give the CO_2 profile of Figure 2.



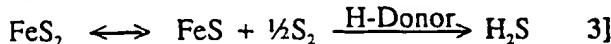
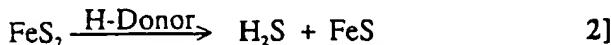
Figures 1 and 2. Gas evolution profiles showing the impact of carbonate minerals on Illinois #6 coal pyrolysis at 10 K/min heating rate.

Table 1. Reactions controlling H_2S evolution.

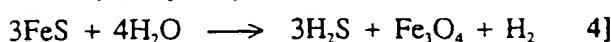
I. Formation from (A) Organics:



(B) Pyrite:



(C) Hydrolysis:



II. Capture by (A) Minerals (M = Fe):



(B) Organic Intermediates:



Table 1 lists the set of reactions that apply to H_2S evolution from Illinois #6 coal. To simplify the complicated chemistry, we can use acid-leached coal and eliminate reaction 5]. Those experiments using coal free of carbonates proved most informative. We define pyrite as FeS_2 , recognizing that FeS_2 in coal has several forms and the name is imprecise. Highly crystalline FeS_2 and a specially prepared frambooidal material⁷ behaved similarly as additives in the work described, if air oxidation was carefully avoided.

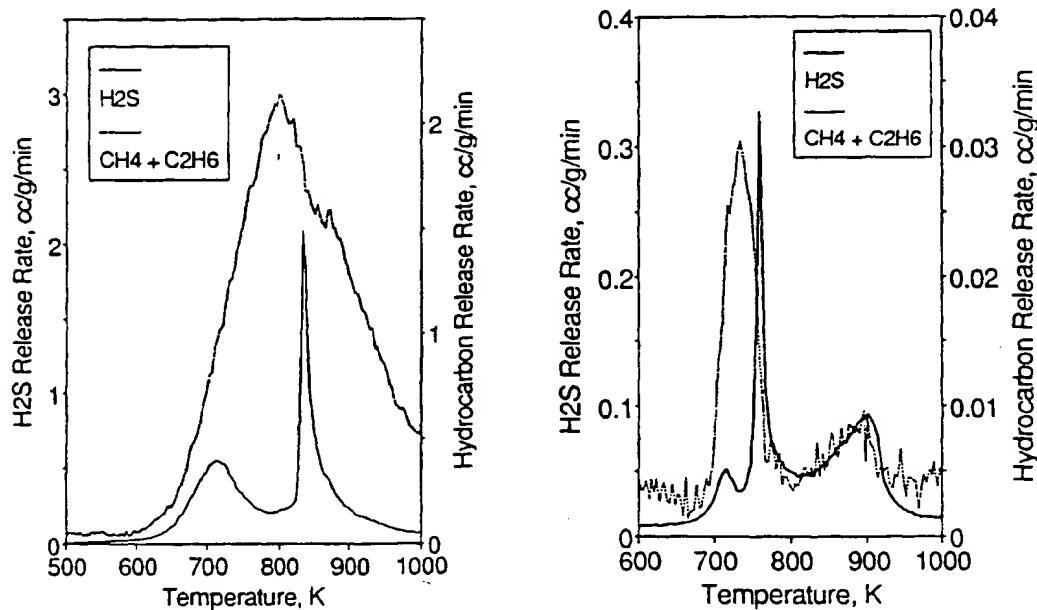
A first thought on viewing Figure 1 is that low temperature H_2S release from coal is due to

decomposition of organic sulfur compounds (reaction 1]) and that high temperature release is due to pyrite decomposition (reactions 2] or 3]). However, it is well established that pyrite contributes to both low and high temperature release.^{1,2} Khan² writes the following expression for $[H_2S]$ on heating various coals to 773 K under his experimental conditions:

$$[H_2S] = 0.17(\text{Coal}_{\text{Pyr-S}}) + 0.40(\text{Coal}_{\text{Org-S}}); \quad R^2 = 0.94 \quad 7]$$

By default, reaction 2] seems to best characterize low temperature formation of H_2S from pyrite. It is a surface reaction that depends on the availability of *in-situ* generated H-donors. A shrinking core model with the rate of iron migration toward crystallite interiors controlling the quantity of active sulfur at the interface^{3,9} fits the data. Both reaction 1] and 2] require H-donors formed from the coal, so inorganic and organic sources of H_2S are coupled. Furthermore, hydrocarbon formation competes for donors (reaction 6]). Methane-plus-ethane, the principal hydrocarbons released from coal, can be used to follow this competing reaction. Since methane release signifies re-solidification of a plastic coal,¹⁰ H-donor mobility also may diminish in this temperature range. H_2S added to the sweep gas was not captured, indicating condensed phase chemistry.

As acid-leached coal heats up, H-donors form, generating H_2S until organic free radical precursors of gas and tar become so abundant that they consume most of the mobile H-donor capacity (Figure 3). H_2S release then drops off. At about 830 K, a new pyrite decomposition reaction dominates, unimolecular decomposition, reaction 3]. Active sulfur forms and reacts aggressively with hydrogen-donors or hydrocarbon precursors (note an inflection at 830 K in the CH_4 -plus- C_2H_6 curve of Figure 3). The sharp decomposition occurs just at the temperature where pyrite decomposes in a vacuum (with a rate equal to 0.07 mg-S/cm²/min at 773 K).⁸ Coal pyrolysis products remove sulfur effectively, and the reverse reaction is eliminated. High temperature H_2S release thus occurs at a lower temperature than from pure pyrite in a TGA apparatus under 1 atmosphere of inert gas.



Figures 3 and 4. Evidence for the competition with organic free radicals for H-donors: (3) Acid-leached III #6 and (4) polystyrene/pyrite/firebrick pyrolysis.

It should be possible to see the two pyrite decomposition modes in simpler systems. An inert mineral phase (firebrick), a pure organic phase with no organic sulfur (polystyrene), and analytically pure pyrite with no air contact would be the ideal case. Figure 4 shows that under our standard pyrolysis conditions this ideal system does result in two H₂S releases with a minimum at the CH₄-plus-C₂H₆ maximum-release temperature. A distinct H₂S loss as pyrrhotite becomes increasingly stoichiometric also is seen in Figure 4. This reaction merges into the broad organic H₂S release when coal pyrolyzes. Results of Figures 3 and 4 are generally consistent, although hydrocarbons and hydrogen-donors form over a narrower temperature range in our "ideal" system.

The high temperature H₂S release peak is so narrow that dispersion and detector sampling frequency affect its appearance. Charring and reaction 4] distort the peak. The surface layer of inorganic sulfides form by capture of H₂S seems particularly susceptible to hydrolysis. Sweep with dry argon, water-saturated argon, and steam give significantly different high temperature H₂S releases. Both the absolute quantity of water (degree of dilution) and the [H₂S]:[H₂O] ratio matter. Water sources include reaction 5], the water gas shift reaction, and illite dehydration.

The variety of reactions in Table 1 offer opportunities to adjust H₂S evolution during coal pyrolysis within a limited range. Water, reactive solids, and organic intermediates all interact with H₂S or H₂S precursors to an extent that depends on reaction conditions, coal type, and the details of the pyrolysis process.

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